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(54) Title: SOLUTION PHASE POLYMERIZATION PROCESS UTILIZING METALLOCENE CATALYST WITH PRODUCTION OF OLEFIN POLYMERS (57) Abstract The present invention relates to a solution phase polymerization process utilizing mono and dicyclopentadienyl transition metal components activated by and alumoxane or a noncoordinating anion for the production of olefin polymers and copolymers. By appropriate selection of the metallocene and activator components the catalyst system can be tailored to produce a particular weight average molecular weight (M_w) polyolefins of a select tacticity type.		

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SOLUTION PHASE POLYMERIZATION PROCESS UTILIZING
METALLOCENE CATALYST WITH PRODUCTION OF OLEFIN
POLYMERS

5 Field of the Invention

This invention relates to a solution phase polymerization utilizing metallocene catalyst(s) for the polymerization of olefins. In particular, this invention relates to a single or multiple reactor process for olefin polymerization using metallocene catalyst(s). This invention further relates to multiple reactors in series or in parallel operating at similar or different process conditions utilizing metallocene catalyst(s) for olefin polymerization. In addition, the invention contemplates homopolymers and copolymers of olefins particularly α -olefins and more particularly ethylene and/or propylene copolymers with comonomers of up to C₁₀₀ olefins. This invention further contemplates terpolymers of a mixture of any three olefins from C₂ to C₁₀₀. The polymers of this can be crystalline, semi-crystalline or amorphous products that may include long chain branching. Metallocene catalysts and a cocatalyst activator are utilized herein to polymerize the olefins.

25 Background of the Invention

Solution processes have some unique advantages over slurry processes. The molecular weight distribution and the process variables are more easily controlled because the polymerization occurs in a homogeneous phase. The high

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polymerization temperature typically up to 160°C also leads to high reaction rates and high polymer throughputs from the reactor. However, very high molecular weights cannot be processed easily at these high temperatures and since the solids content is relatively low compared with the slurry process and greater diluent recovery may be required. Due to its high energy requirement, the solution process is used primarily for the production of relatively low molecular weight resins which are difficult to manufacture by the liquid slurry or gas phase processes. For example, injection molding grade high density polyethylene having low molecular weight and narrow molecular distribution is typically obtained by the solution process. Also high temperature favors low molecular weight products. It has been reported that the solution process is most efficient for production of low molecular weight resins. Solution process is thought much less satisfactory for higher molecular weight resins because of the excessive viscosity in the reactor as discussed by Choi and Ray, JMS Review Macromolecular Chemical Physics C25(1), 1-55, pg. 10 (1985).

Typically, in the solution process, the monomer and polymer are dissolved in an inert solvent and the polymer product is recovered as a hot melt that is fed directly into the extrusion or pelletizing equipment. Unlike the gas phase or slurry process there is usually no polymer solid or powder formed. Typically, the reaction

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temperature and the reaction pressure are higher than in gas phase or slurry process to maintain the polymer in solution. The solution process tends to use an inert solvent that dissolves the polymer as it is formed, subsequently the solvent is evaporated and the polymer is pelletized. The heat needed to melt the polymer comes from the heat of reaction. The solution process is considered versatile in that a wide spectrum of product properties can be obtained by varying the Ziegler type catalyst recipe, the pressure, the temperature and the comonomer employed. Since relatively small reactors are used, residence time is short and grade change over can be rapid.

In particular, it is known that Dow Chemical produces ethylene/octene-1 copolymer as a VLDPE. It is believed that Dow uses two reactors in series operated at pressures of up to 750 psi (≈5200 kPa) and up to 250°C in the reactor. Fresh and recycled ethylene is compressed up to 800 psig (≈5500 kPa) and pumped into the polymerization reactor by a feed pump. The reaction is adiabatic and maintained at a maximum reactor outlet of about 250°C. Although a single reactor can be used, it is believed that the multiple reactors provide a good control of molecular weight distribution. The Dow process is believed to use a high activity Ziegler catalyst of a titanium halide complex with an aluminum alkyl.

Indeed, the shift in polyethylene manufacturing technology from traditional high pressure radical production to low pressure

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Ziegler production has created many new families of polyethylenes ranging from high density (with little or no comonomer) to low density (LLDPE which has a uniform incorporation of comonomers to suppress crystallinity). These new materials can be designed for specific uses and, for the most part, outperform LDPE (with its randomly branched structure). Exceptions, where LDPE still is the material of choice, are applications which benefit from the unique melt properties imparted to LDPE by virtue of its long-chain branched structure.

This invention represents a method to introduce long chain branching into linear polyolefins like HDPE and LLDPE in a controllable fashion. The branches are introduced through ethylene or propylene copolymerization with polymeric monomers, which are themselves polyolefins prepared under conditions that gives a high concentration of chain-ends with vinyl unsaturation.

The possibility that LCB (long chain branching) occurs in Ziegler prepared polymers was first recorded by F.P. Baldwin and G. ver Strate Rubber Chem and Tech Vol 45 No 3 (1972). This early work speculated that a "spontaneous" termination process could occur which yield a active or inactive catalyst and an olefin terminated polymer. This olefin terminated polymer could then copolymerize to give the branched olefin.

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This early hypothesis has not enabled prior researchers in LCB polyolefins to produce branched polyolefins.

5 Nippon Oil (07.03.86-JP-048525) uses a two stage polymerization process: chromium containing solid catalyst in the first and titanium/magnesium in the second to produce polymers have improved processibility and a wide MWD; no mention of LCB is made in the patent. Metallocene catalysts with
10 cocatalyst activators of non-coordinating anions or an alumoxane have striking differences over prior Ziegler-Natta and other catalysts. Among many of these differences include the ability to tailor molecular weight distribution to very
15 narrow amounts and uniform composition distribution within the polymer chain. These unique abilities, among others, lead to a multitude of final product properties that are different and superior to those known before. For
20 example, a particular polyethylene made with a bis-cyclopentadienyl Group 4 transition metal compound and a methylalumoxane is stronger and clearer than known polyethylene.

Thus, there exists in the art a need for a
25 solution phase reactor process that utilizes metallocene catalyst(s) to produce tailored polymer products.

Summary of the Invention

30 This invention relates to a solution phase polymerization process utilizing metallocene catalysts to produce olefin polymers. In particular, this solution phase process utilizes

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metallocene catalysts with cocatalysts activators of the alumoxane or noncoordinating anion type. The metallocene catalyst is an activated cyclopentadienyl transition metal compound and the

5 transition metal is from group 4 of the Periodic Table of Elements. In particular, the catalysts employed in this invention are organometallic coordination compounds which are cyclopentadienyl derivatives of group 4 metals of the periodic

10 table of the elements and include mono-, di- and tri-cyclopentadienyls and their derivatives of the transition metals. Particularly desirable are the metallocenes of the group 4 metal such as titanium, zirconium and hafnium. The

15 cyclopentadienyl metallocenes of this invention can be activated with either an alumoxane or a non-coordinating anion type activator. In general at least one metallocene compound is employed in formation of the catalyst. The metallocenes

20 usefully employed in accordance with this invention contain at least one cyclopentadienyl ring. The metal is selected from group 4 preferably titanium, zirconium and hafnium most preferably hafnium and zirconium for

25 bicyclopentadienyl compound and titanium for monocyclopentadienyl compound. The cyclopentadienyl ring can be substituted or unsubstituted or contain one or more substituents e.g. from 1 to 5 substituents such as for example,

30 hydrocarbyl substituent e.g. up to five C₁ to C₂₀ hydrocarbyl substituents or other substituents e.g. for example, a trialkyl cyclic substituent.

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A metallocene can contain 1, 2 or 3 cyclopentadienyl rings, however, two rings are preferred for use with hafnium and zirconium. One ring is preferred for use with titanium.

5 Detailed Description

This invention relates to a solution phase polymerization process utilizing metallocene catalysts to produce olefin polymers. In particular, this solution phase process utilizes
10 metallocene catalysts with cocatalysts activators of the alumoxane or noncoordinating anion type.

Ionic Catalyst System - General Description

The process of this invention is practiced with that class of ionic catalysts referred to, disclosed, and described in copending U.S. Patent
15 Application Serial Nos. 133,052; 133,480; and 542,236, and U.S. Patents 5,055,438 and 5,096,867. The ionic catalysts used in this invention can be represented by one of the following general
20 formulae (all references to groups being the new group notation of the Period Table of the Elements as described by Chemical and Engineering News, 63(5), 27, 1985):

1. $[[[(A-Cp)MX_1]^+]_d] ([B']^{d-})$
 2. $[[[(A-Cp)MX_1L]^+]_d] ([B']^{d-})$
 3. $\left\{ \left[\begin{array}{c} (C_5H_5-\gamma-xS_x) \\ \diagdown \quad \diagup \\ (A')_y \quad M \\ \diagup \quad \diagdown \\ (JS'_{z-1-y}) \end{array} \right]^+ (L')_w X_1 \right\} ([B']^{d-})_d$
- wherein:

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(A-Cp) is either (Cp) (Cp*) or Cp-A'-Cp*; Cp and Cp* are the same or different cyclopentadienyl rings substituted with from zero to five substituent groups S, each substituent group S being, independently, a radical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted pnictogen, substituted chalcogen or halogen radicals, or Cp and Cp* are cyclopentadienyl rings in which any two adjacent S groups are joined forming a C₄ to C₂₀ ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

A' is a bridging group, which group may serve to restrict rotation of the Cp and Cp* rings or (C₅H₅-y-xS_x) and JS'(z-1-y) groups;

(C₅H₅-y-xS_x) is a cyclopentadienyl ring substituted with from zero to five S radicals;

x is from 1 to 5 denoting the degree of substitution;

M is titanium, zirconium or hafnium;

X₁ is a hydride radical, hydrocarbyl radical, substituted-hydrocarbyl radical, hydrocarbyl-substituted organometalloid radical or halocarbyl-substituted organometalloid radical which radical may optionally be covalently bonded to both or either M and L or all or any M, S or S';

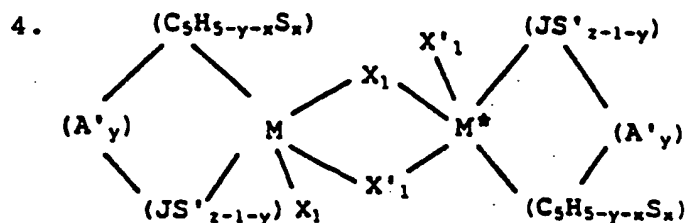
(JS_{z-1-y}) is a heteroatom ligand in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an

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element from Group 16 with a coordination number of 2; S is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid; and z is the coordination number of the element J;

y is 0 or 1;

L is an olefin, diolefin or aryne ligand, or a neutral Lewis base; L' can also be a second transition metal compound of the same type such that the two metal center M and M* are bridged by X₁ and X'₁, wherein M* has the same meaning as M and X'₁ has the same meaning as X₁ where such dimeric compounds which are precursors to the cationic portion of the catalyst are represented by the formula:



w is an integer from 0 to 3;

B is a chemically stable, non-nucleophilic anionic complex having a molecular diameter about or greater than 4 angstroms or an anionic Lewis-acid activator resulting from the reaction of a Lewis-acid activator with the precursor to the cationic portion of the catalyst system described in formulae 1-4. When B' is a Lewis-acid

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activator, X_1 can also be an alkyl group donated by the Lewis-acid activator; and

d is an integer representing the charge of B.

The improved catalysts are preferably
5 prepared by combining at least two components. In one preferred method, the first component is a cyclopentadienyl derivative of a Group 4 metal compound containing at least one ligand which will combine with the second component or at least a
10 portion thereof such as a cation portion thereof. The second component is an ion-exchange compound comprising a cation which will irreversibly react with at least one ligand contained in said Group 4 metal compound (first component) and a non-
15 coordinating anion which is either a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central formally charge-bearing metal or metalloid atom or an anion comprising a
20 plurality of boron atoms such as polyhedral boranes, carboranes and metallocarboranes.

In general, suitable anions for the second component may be any stable and bulky anionic complex having the following molecular attributes:
25 1) the anion should have a molecular diameter greater than 4 Å; 2) the anion should form stable ammonium salts; 3) the negative charge on the anion should be delocalized over the framework of the anion or be localized within the core of the
30 anion; 4) the anion should be a relatively poor nucleophile; and 5) the anion should not be a powerful reducing to oxidizing agent. Anions

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meeting these criteria - such as polynuclear boranes, carboranes, metallacarboranes, polyoxoanions and anionic coordination complexes are well described in the chemical literature.

5 The cation portion of the second component may comprise Bronsted acids such as protons or protonated Lewis bases or may comprise reducible Lewis acids such as ferricinium, tropylium, triphenylcarbenium or silver cations.

10 In another preferred method, the second component is a Lewis-acid complex which will react with at least one ligand of the first component, thereby forming an ionic species described in formulae 1-4 with the ligand abstracted from the
15 first component now bound to the second component. Alumoxanes and especially methylalumoxane, the product formed from the reaction of trimethylaluminum in an aliphatic or aromatic hydrocarbon with stoichiometric quantities of
20 water, are particularly preferred Lewis-acid second components.

 Upon combination of the first and second components, the second component reacts with one of the ligands of the first component, thereby
25 generating an anion pair consisting of a Group 4 metal cation and the aforementioned anion, which anion is compatible with and noncoordinating towards the Group 4 metal cation formed from the first component. The anion of the second compound
30 must be capable of stabilizing the Group 4 metal cation's ability to function as a catalyst and must be sufficiently labile to permit displacement

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by an olefin, diolefin or an acetylenically unsaturated monomer during polymerization. The catalysts of this invention may be supported. U.S. Patents 4,808,561, issued 2-28-89; 4,897,455
5 issued 1-3-90; 5,057,475 issued 10-15-91; and U.S. Patent Application 459,921 (published as PCT International publication WO 91/09882)

disclose such supported catalysts and the methods to produce such and are herein incorporated by
10 reference.

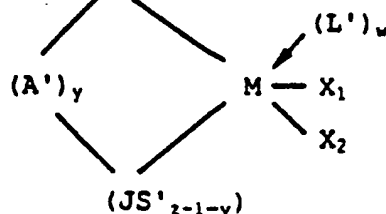
A. The Metallocene Component

The Group 4 metal compounds; i.e., titanium, zirconium and hafnium metallocene compounds, useful as first compounds in the preparation of
15 the improved catalyst of this invention are cyclopentadienyl derivatives of titanium, zirconium and hafnium. In general, useful titanocenes, zirconocenes and hafnocenes may be represented by the following general formulae:

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5. $(A-Cp)MX_1X_2$
6. $(A-Cp)ML$
7. $(Cp^*)(CpR)MX_1$
8. $(C_5H_5-y-xS_x)$

5



10 wherein:

$(A-Cp)$ is either (Cp) (Cp^*) or $Cp-A'-Cp^*$; Cp and Cp^* are the same or different cyclopentadienyl rings substituted with from zero to five substituent groups S , each substituent group S being, independently, a radical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted pnictogen, substituted chalcogen or halogen radicals, or Cp and Cp^* are cyclopentadienyl rings in which any two adjacent S groups are joined forming a C_4 to C_{20} ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

25

R is a substituent on one of the cyclopentadienyl radicals which is also bonded to the metal atom;

A' is a bridging group, which group may serve to restrict rotation of the Cp and Cp^* rings or $(C_5H_5-y-xS_x)$ and $JS'_{(z-1-y)}$ groups;
 y is 0 or 1;

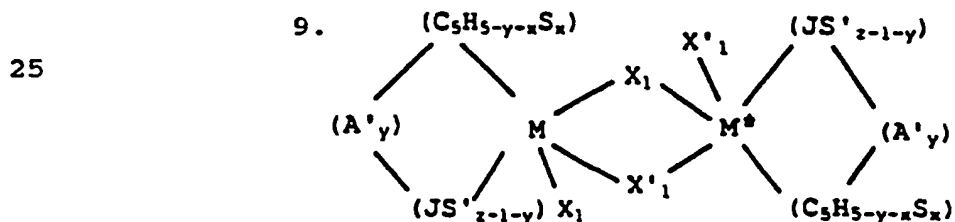
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$(C_5H_5-y-xS_x)$ is a cyclopentadienyl ring substituted with from zero to five S radicals; x is from 1 to 5 denoting the degree of substitution;

5 (JS'_{z-1-y}) is a heteroatom ligand in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an element from Group 16 with a coordination number of 2, S is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted
10 halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid; and z is the coordination number of the element J;

15 L is an olefin, diolefin or aryne ligand, or a neutral Lewis base; L' can also be a second transition metal compound of the same type such that the two metal centers M and M* are bridged by X_1 and X'_1 , wherein M* has the same meaning as M and X'_1 has the same meaning as X_1 where such
20 dimeric compounds which are precursors to the cationic portion of the catalyst are represented by the formula:



30 w is an integer from 0 to 3; and X_1 and X_2 are, independently, hydride radicals, hydrocarbyl radicals, substituted

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hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals, substituted pnictogen radicals, or substituted chalcogen radicals; or X_1 and X_2 are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; or X_1 and X_2 together can be an olefin, diolefin or aryne ligand; or when Lewis-acid activators are used, X_1 and X_2 can also be joined to form an anionic chelating ligand.

Table 1 depicts representative constituent moieties for the metallocene components of formulae 6-9. The list is for illustrative purposes only and should not be construed to be limiting in any way. A number of final components may be formed by permuting all possible combinations of the constituent moieties with each other. Illustrative compounds of the formula 6 type are: bis(cyclopentadienyl)hafnium dimethyl, ethylenebis(tetrahydroindenyl)zirconium dihydride, bis(pentamethyl)zirconium ethylidene, dimethylsilyl(1-fluorenyl)(cyclopentadienyl)titanium dichloride and the like. Illustrative compounds of the formula 7 type are: bis(cyclopentadienyl) (1,3-butadiene(zirconium)), bis(cyclopentadienyl) (2,3-dimethyl-1,3-butadiene) zirconium, bis(pentamethylcyclopentadienyl) (benzene) zirconium, bis(pentamethylcyclopentadienyl) titanium ethylene and the like. Illustrative compounds of the formula 8 type are:

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(pentamethylcyclopentadienyl)
(tetramethylcyclopentadienylmethylene) zirconium
hydride, (pentamethylcyclopentadienyl)
(tetramethylcyclopentadienyl)-

5 (tetramethylcyclopentadienylmethylene) zirconium
phenyl and the like. Illustrative compounds of
the formula 9 type are:

dimethylsilyl(tetramethylcyclopentadienyl) (t-
butylamido)zirconium dichloride,
10 ethylene(methylcyclopentadienyl)
(phenylamido)titanium dimethyl,
methylphenylsilyl(indenyl) (phenylphosphido)hafnium
dihydride and (pentamethylcyclopentadienyl) (di-t-
butylamido)hafnium dimethoxide.

15 For illustrative purposes, the above
compounds and those permuted from Table 1 include
the neutral Lewis base ligand (L'). The
conditions under which complexes containing
neutral Lewis base ligands such as ether or those
20 which form dimeric compounds is determined by the
steric bulk of the ligands about the metal center.
For example, the t-butyl group in $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrCl}_2$ has greater steric requirements than
the phenyl group in $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{NPh})\text{ZrCl}_2 \cdot \text{Et}_2\text{O}$
25 thereby not permitting ether coordination in the
former compound in its solid state. Similarly,
due to the decreased steric bulk of the
trimethylsilylcyclopentadienyl group in
[$\text{Me}_2\text{Si}(\text{Me}_3\text{SiC}_5\text{H}_3)(\text{N-t-Bu})\text{ZrCl}_2$]₂ versus that of
30 the tetramethylcyclopentadienyl group in
 $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrCl}_2$, the former compound is
dimeric and the latter is not.

TABLE 1

A'	Cp, Cp*, CpR or (C ₄ H ₅ -x-y-z-S _y)	(JS', z)	X ₁ or X ₂	M
dimethylsilyl	cyclopentadienyl	t-butylamido	hydride	zirconium
diethylsilyl	methylcyclopentadienyl	phenylamido	methyl	hafnium
di-n-propylsilyl	1,2-dimethylcyclopentadienyl	p-n-butylphenylamido	ethyl	titanium
diisopropylsilyl	1,3-dimethylcyclopentadienyl	cyclohexylamido	phenyl	Group 5 TM
di-n-butylsilyl	indenyl	perfluorophenylamido	n-propyl	Group 6 TM
di-t-butylsilyl	1,2-diethylcyclopentadienyl	n-butylamido	isopropyl	
di-n-hexylsilyl	tetramethylcyclopentadienyl	methylamido	n-butyl	L or L'
methylphenylsilyl	ethylcyclopentadienyl	ethylamido	amyl	ethylene
ethylmethylsilyl	n-butylcyclopentadienyl	n-propylamido	isoamyl	propylene
diphenylsilyl	cyclohexylmethylcyclopentadienyl	isopropylamido	hexyl	1-butene
di(p-t-butylphenethylsilyl)	n-octylcyclopentadienyl	benzylamido	isobutyl	1,4-hexadiene
n-hexylmethylsilyl	beta-phenylpropylcyclopentadienyl	t-butylphosphido	heptyl	1,3-butadiene
cyclopentamethylenesilyl	tetrahydroindenyl	ethylphosphido	octyl	1,3-hexadiene
cyclohexamethylenesilyl	propylcyclopentadienyl	phenylphosphido	nonyl	acetylene
cyclooctamethylenesilyl	t-butylcyclopentadienyl	cyclohexylphosphido	decyl	methyl-acetylene
dimethylgermyl	benzylcyclopentadienyl	oxo	cetyl	ethylacetylene
diethylgermyl	diphenylmethylcyclopentadienyl	sulfido	methylidene (both X)	benzynes
phenylamido	trimethylgermylcyclopentadienyl		ethylidene (both X)	
t-butylamido	trimethylstannylcyclopentadienyl	JS' (z=1-y)	ethylidene (both X)	L'
methylamido	triethylplumbylcyclopentadienyl	methoxido		diethylether
t-butylphosphido	trifluoromethylcyclopentadienyl	ethoxido		dimethylether
ethylphosphido	trimethylsilylcyclopentadienyl	methylthio		trimethylamine
phenylphosphido	pentamethylcyclopentadienyl (when y = 0)	ethylthio		triphenylamine
methylene	fluorenyl			triethylamine
dimethylmethylene	octahydrofluorenyl			triphenyl-phosphine
diethylmethylene	N,N-dimethylamidocyclopentadienyl			tetrahydrofuran
ethylene	dimethylphosphidocyclopentadienyl			thiophene
dimethylethylene	methoxycyclopentadienyl			dimethyl-sulfide

TABLE 1 (CONT'D)

A'	Cp, Cp* CpR or (C ₅ H ₅ -x-S _x) (H, H-dimethylamidomethyl)cyclopentadienyl
dipropylethylene	
propylene	
dimethylpropylene	
diethylpropylene	
1,1-dimethyl-3,3-	
dimethylpropylene	
tetramethyldisiloxane	
1,1,4,4-	
tetramethyldisilylethylene	

SUBSTITUTE SHEET

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B. The Activator Component

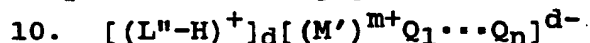
Ionic catalysts can be prepared by reacting a transition metal compound with some neutral Lewis acids, such as $B(C_6F_5)_3$ or an alumoxane, which upon reaction with the hydrolyzable ligand (X) of the transition metal compound forms an anion, such as $[B(C_6F_5)_3(X)]^-$, which stabilizes the cationic transition metal species generated by the reaction. Ionic catalysts can be, and preferably are, prepared with activator components which are ionic compounds or compositions.

Compounds useful as an activator component in the preparation of the ionic catalyst systems used in the process of this invention comprise a cation, which is preferably a Bronsted acid capable of donating a proton, and a compatible non-coordinating anion which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group 4 cation) which is formed when the two compound are combined and said anion will be sufficiently labile to be displaced by olefinic diolefinic and acetylenically unsaturated substrates or other neutral Lewis bases such as ethers, nitriles and the like. Two classes of compatible non-coordinating anions have been disclosed in copending U.S. Patent Application Nos. 133,052 and 133,480: 1) anionic coordination complexes comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid core, and 2) anions comprising a

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plurality of boron atoms such as carboranes, metallacarboranes and boranes.

In general, the activator compounds containing single anionic coordination complexes which are useful in this invention may be represented by the following general formula:



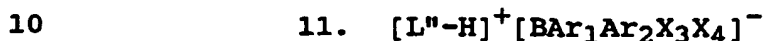
wherein:

- H is a hydrogen atom;
 - 10 $[L''-H]$ is a Bronsted acid;
 - M' is a metal or metalloid;
 - Q₁ to Q_n are, independently, bridged or unbridged hydride radicals, dialkylamido radicals, alkoxide and aryloxy radicals, hydrocarbyl and substituted-hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals and hydrocarbyl and halocarbyl-substituted organometalloid radicals and any one, but not more than one, of Q₁ to Q_n may be a halide radical;
 - 20 m is an integer representing the formal valence charge of M; and
 - n is the total number of ligands q.
- As indicated above, any metal or metalloid capable of forming an anionic complex which is stable in water may be used or contained in the anion of the second compound. Suitable metals, then, include, but are not limited to, aluminum, gold, platinum and the like. Suitable metalloids include, but are not limited to, boron, phosphorus, silicon and the like. Compounds containing anions which comprise coordination complexes containing a single metal or metalloid

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atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially. In light of this, salts containing
5 anions comprising a coordination complex containing a single boron atom are preferred.

The preferred activator compounds comprising boron may be represented by the following general formula:



wherein:

B is a boron in a valence state of 3;

Ar₁ and Ar₂ are the same or different aromatic or substituted-aromatic hydrocarbon
15 radicals containing from about 6 to about 20 carbon atoms and may be linked to each other through a stable bridging group; and

X₃ and X₄ are, independently, hydride radicals, hydrocarbyl and substituted-hydrocarbyl
20 radicals, halocarbyl and substituted-halocarbyl radicals, hydrocarbyl- and halocarbyl-substituted organometalloid radicals, disubstituted pnictogen radicals, substituted chalcogen radicals and halide radicals, with the proviso that X₃ and X₄
25 will not be halide at the same time.

In general, Ar₁ and Ar₂ may, independently, be any aromatic or substituted-aromatic hydrocarbon radical. Suitable aromatic radicals include, but are not limited to, phenyl, naphthyl
30 and anthracenyl radicals. Suitable substituents on the substituted-aromatic hydrocarbon radicals, include, but are not necessarily limited to,

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hydrocarbyl radicals, organometalloid radicals, alkoxy and aryloxy radicals, alkylamido radicals, fluorocarbyl and fluorohydrocarbyl radicals and the like such as those useful as X_3 and X_4 . The substituent may be ortho, meta or para, relative to the carbon atoms bonded to the boron atom. When either or both X_3 and X_4 are a hydrocarbyl radical, each may be the same or a different aromatic or substituted-aromatic radical as are Ar_1 and Ar_2 , or the same may be a straight or branched alkyl, alkenyl or alkynyl radical, a cyclic hydrocarbon radical or an alkyl-substituted cyclic hydrocarbon radical. X_3 and X_4 may also, independently be alkoxy or dialkylamido radicals wherein the alkyl portion of said alkoxy and dialkylamido radicals, hydrocarbyl radicals and organometalloid radicals and the like. As indicated above, Ar_1 and Ar_2 could be linked to either X_3 or X_4 . Finally, X_3 and X_4 may also be linked to each other through a suitable bridging group.

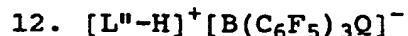
Illustrative, but not limiting, examples of boron compounds which may be used as an activator component in the preparation of the improved catalysts of this invention are trialkyl-substituted ammonium salts such as triethylammonium tetra(phenyl)boron, tripropylammonium tetra(phenyl)boron, tri(n-butyl)ammonium tetra(phenyl)boron, trimethylammonium tetra(p-tolyl)boron, trimethylammonium tetra(o-tolyl)boron, tributylammonium tetra(pentafluorophenyl)boron,

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tripropylammonium tetra(o,p-dimethylphenyl)boron,
tributylammonium tetra(m,m-dimethylphenyl)boron,
tributylammoniumtetra(p-tri-
fluoromethylphenyl)boron, tri(n-butyl)ammonium
5 tetra(o-tolyl)boron and the like; N,N-dialkyl
anilinium salts such as N,N-dimethylanilinium
tetra(pentafluorophenyl)boron, N,N-di-
ethylanilinium tetra(phenyl)boron, N,N-2,4,5-
pentamethylanilinium tetra(phenyl)boron and the
10 like; dialkyl ammonium salts such as di(i-
propyl)ammonium tetra(pentafluorophenyl)boron,
dicyclohexylammonium tetra(phenyl)boron and the
like; and triaryl phosphonium salts such as
triphenylphosphonium tetra(phenyl)boron,
15 tri(methylphenyl)phosphonium tetra(phenyl)boron,
tri(dimethylphenyl)phosphonium tetra(phenyl)boron
and the like.

Similar lists of suitable compounds
containing other metals and metalloids which are
20 useful as activator components may be made, but
such lists are not deemed necessary to a complete
disclosure. In this regard, it should be noted
that the foregoing list is not intended to be
exhaustive and that other useful boron compounds
25 as well as useful compounds containing other
metals or metalloids would be readily apparent to
those skilled in the art from the foregoing
general equations.

The most preferred activator compounds
30 comprising boron may be represented by the
following general formula:



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wherein:

F is fluorine, C is carbon and B, L', and Q are defined hereinabove. Illustrative but not limiting, examples of most preferred activator compounds comprising boron which may be used in the preparation of the improved catalysts of this invention include N,N-dialkylanilinium salts (L' = N,N-dialkylaniline) where Q is a simple hydrocarbyl such as methyl, butyl, cyclohexyl, or phenyl or where Q is a polymeric hydrocarbyl of indefinite chain length such as polystyrene, polyisoprene, or poly-paramethylstyrene. Polymeric Q substituents on the most preferred anion offer the advantage of providing a highly soluble ion-exchange activator component and final ionic catalyst. Soluble catalysts and/or precursors are often preferred over insoluble waxes, oils, phases, or solids because they can be diluted to a desired concentration and can be transferred easily using simple equipment in commercial processes.

Activator components based on anions which contain a plurality of boron atoms may be represented by the following general formulae:

- 25 13. $[L''-H]_c[(CX)_a(BX)_mX_b]^{c-}$ or
 14. $[L''-H]_d'[[[(CX)_6]_a'(BX)_7]_m'(X_8)_b']^{c'-}]_2M^{n'+}]^{d'-}$
 wherein

[L''-H] is either H^+ or a Bronsted acid derived from the protonation of a neutral Lewis base;

30 X, X', X'', X₆, X₇ and X₈ are, independently, hydride radicals, halide radicals, hydrocarbyl

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radicals, substituted-hydrocarbyl radicals, halocarbyl radicals, substituted-halocarbyl radicals, or hydrocarbyl- or halocarbyl-substituted organometalloid radicals;

5 M is a transition metal;

a and b are integers ≥ 0 ; c is an integer ≥ 1 ; $a + b + c =$ an even-numbered integer from 2 to about 8; and m is an integer ranging from 5 to about 22;

10 a and b are the same or a different integer 0; c is an integer ≥ 2 ; $a + b + c =$ an even-numbered integer from 4 to about 8; m is an integer from 6 to about 12; n is an integer such that $2c - n = d$; and d is an integer ≥ 1 .

15 Preferred anions of this invention comprising a plurality of boron atoms comprise:

(1) A trisubstituted ammonium salt of a borane or carborane anion satisfying the general formula:

20 15. $[(CH)_{ax}(BH)_{bx}]^{cx-}$

wherein:

ax is either 0 or 1; cx is either 1 or 2; $ax + cx = 2$; and bx is an integer ranging from about 10 to 12;

25 (2) A trisubstituted ammonium salt of a borane or carborane or a neutral borane or carborane compound satisfying the general formula:

16. $[(CH)_{ay}(BH)_{my}(H)_{by}]^{cy-}$

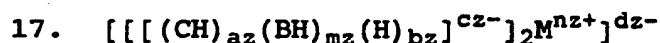
wherein:

30 ay is an integer from 0 to 2; by is an integer from 0 to 3; cy is an integer from 0 to 3;

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ay + by + cy = 4; and my is an integer from about 9 to about 18; or

(3) A trisubstituted ammonium salt of a metallaborane or metallocarborane anion satisfying the following general formula:



wherein:

az is an integer from 0 to 2; bz is an integer from 0 to 2; cz is either 2 or 3; mz is an integer from about 9 to 11; az + bz + cz = 4; and nz and dz are, respectively, 2 and 2 or 3 and 1.

Illustrative, but not limiting, examples of second components which can be used in preparing catalyst systems utilized in the process of this invention wherein the anion of the second component contains a plurality of boron atoms (as in formulae 10-17) are mono-, di-, trialkylammonium and phosphonium and dialkylarylammonium and -phosphonium salts such as bis[tri(n-butyl)ammonium] dodecaborate, bis[tri(n-butyl)ammonium]decachlorododecaborate, tri(n-butyl)ammonium dodecachlorododecaborate, tri(n-butyl)ammonium 1-carbadecaborate, tri(n-butyl)ammonium 1-carbaudodecaborate, tri(n-butyl)ammonium 1-carbadodecaborate, tri(n-butyl)ammonium 1-trimethylsilyl-1-carbadecaborate, tri(n-butyl)ammonium dibromo-1-carbadodecaborate; borane and carborane complexes and salts of borane and carborane anions such as decaborane(14), 7,8-dicarbaudodecaborane(13), 2,7-dicarbaundodecaborane(13), undecahydrido-7,8-dimethyl-7,8-dicarbaundodecaborane, tri(n-

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butyl)ammonium 6-carbadecaborate(12), tri(n-butyl)ammonium 7-carbaundecaborate, tri(n-butyl)ammonium 7,8-dicarbaundecaborate and metallaborane anions such as tri(n-butyl)ammonium

5 bis(nonahydrido-1,3-dicarbanonaborato)cobaltate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundecaborato)ferrate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundecaborato)

10 cobaltate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaunaborato)nikelate(III), tri(n-butyl)ammonium bis(nonahydrido-7,8-dimethyl-7,8-dicarbaundecaborato)ferrate(III), tri(n-

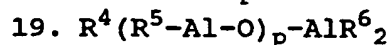
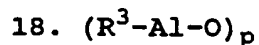
15 butyl)ammonium bis(tribromooctahydrido-7,8-dicarbaundecaborato)cobaltate(III), tri(n-butyl)ammonium bis(undecahydridodicarbadodecaborato)cobaltate(III) and bis[tri(n-butyl)ammonium] bis(undecahydrido-7-carbaundecaborato)

20 cobaltate(III). A similar list of representative phosphonium compounds can be recited as illustrative second compounds, but for the sake of brevity, it is simply noted that the phosphonium and substituted-phosphonium salts corresponding to

25 the listed ammonium and substituted-ammonium salts could be used as second compounds in the present invention.

The preferred activator compounds comprising Lewis-acid activators and in particular alumoxanes

30 are represented by the following general formulae:



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20. $(M')^{m+}Q'_m$

An alumoxane is generally a mixture of both the linear and cyclic compounds. In the general alumoxane formula, R^3 , R^4 , R^5 and R^6 are, independently a C_1 - C_6 alkyl radical, for example, methyl, ethyl, propyl, butyl or pentyl and "p" is an integer from 1 to about 50. Most preferably, R^3 , R^4 , R^5 and R^6 are, each methyl and "p" is a least 4. When an alkyl aluminum halide is employed in the preparation of the alumoxane, one or more R^{3-6} groups may be halide. M' and M are as described previously and Q' is a partially or fully fluorinated hydrocarbyl.

As is now well known, alumoxanes can be prepared by various procedures. For example, a trialkyl aluminum may be reacted with water, in the form of a moist inert organic solvent; or the trialkyl aluminum may be contacted with a hydrated salt, such as hydrated copper sulfate suspended in an inert organic solvent, to yield an alumoxane. Generally, however prepared, the reaction of a trialkyl aluminum with a limited amount of water yields a mixture of both linear and cyclic species of alumoxane.

Suitable alumoxanes which may be utilized in the catalyst systems of this invention are those prepared by the hydrolysis of a trialkylaluminum, such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisobutylaluminum, dimethylaluminum chloride, diisobutylaluminum chloride, diethylaluminum chloride and the like. The most preferred alumoxane for use is

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methylalumoxane (MAO). Methylalumoxanes having an average degree of oligomerization of from about 4 to about 25 ("p" = 4 to 25), with a range of 13 to 25 are the most preferred.

5 It is recognized that an alumoxane is not a discrete material. A typical alumoxane will contain free trisubstituted or trialkyl aluminum, bound trisubstituted or trialkyl aluminum, and alumoxane molecules of varying degree of
10 oligomerization. Those methylalumoxanes most preferred contain lower levels of trimethylaluminum. Lower levels of trimethylaluminum can be achieved by reaction of the trimethylaluminum with a Lewis base or by
15 vacuum distillation of the trimethyl aluminum or any other means known in the art.

 It is also recognized that after reaction with the transition metal compound, some alumoxane molecules are in the anionic form as represented
20 by equations 1-3, and thus for our purposes, are considered "non-coordinating" anions.

 The activator compositions most preferred for forming the ionic catalyst used in this process are those containing a tetrapentafluorophenyl boron
25 anion; two or more tripentafluorophenyl boron anion groups covalently bond to a central atomic molecular or polymeric complex or particle; or methylalumoxane.

 Other examples of activator specific
30 compositions which may be used to form an anionic catalyst useful in this invention are identified and more fully described in European Patent

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Application Nos. 0 277 003 and 0 277 004 and WO 92/00333 which are hereby incorporated by reference.

The Process

- 5 The various catalyst described above are used in a solution process in one to four continuous stirred tank reactor(s) and/or tubular reactor(s) arranged in series or parallel to produce tailored polymer(s). It is specifically contemplated by
- 10 this invention that continuous stirred tank reactors or tubular reactors alone or in combination with one or more other continuous stirred tank or tubular reactors can be used. The continuous stirred tank reactors (CSTR's) or
- 15 tubular reactors (TR's) are operated in series or in parallel and can be operated at the same or different polymerization conditions. In particular, some of the various configurations are:
- 20 (1) CSTR connected in series or parallel to a TR;
(2) a CSTR connected in series or parallel to a TR which is further connected in series or parallel to a CSTR;
(3) a CSTR connected in series or parallel to a TR
- 25 connected in series or parallel to a CSTR
connected in series or parallel to a TR;
(4) a CSTR connected in series or parallel to a CSTR;
(5) a CSTR connected in series or parallel to a TR
- 30 connected in series or parallel to a TR;
(6) three CSTR's connected in series or parallel;
and

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(7) two CSTR's operating in series or parallel. The solution phase polymerization utilizing metallocene catalyst is conducted under reaction conditions. The reactor outlet temperature may be as high as 350°C. The inlet feed temperature can be as low as -40°C. The reactor temperatures are typically maintained at about 250°C, but can be as high as 350°C. The pressure of the reactor can be anywhere up to 5,000 psi (340 atm or), is typically run at 400 to 1500 psi. (1 psi = 6.895 kPa). The composition of the monomer feed can be a uniform composition of monomer in bulk, monomer dissolved in solvents, single monomer dissolved in solvent, multiple monomers dissolved in solvent or multiple monomers in bulk. Indeed, the individual monomers can be present from .001 to 99.999 mole percent depending on the copolymer or terpolymer desired. For example, ethylene and propylene can be mixed with solvent in the monomer feed with monomer ratios of .001 mole percent ethylene to 99.999 mole percent propylene to 99.999 mole percent propylene to .001 mole percent ethylene. When additional monomers are included such that a terpolymer is produced, the termonomer can be present from .0001 to 99.999 mole percent. For example, ethylene, propylene, and a diene could be combined to produce an ethylene/propylene/diene (EPDM) elastomer. Typical dienes for producing EPDM may be non-conjugated dienes such as the following non-limiting examples:

- a. straight chain acyclic dienes such as: 1,4-hexadiene; 1,6-octadiene;

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- b. branched chain acyclic dienes such as: 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; 3,7-dimethyl-1,7-octadiene and mixed isomers of dihydro-myrcene and dihydroocinene;
- 5 c. single ring alicyclic dienes such as: 1,4-cyclohexadiene; 1,5-cyclooctadiene; and 1,5-cyclododecadiene;
- d. multi-ring alicyclic fused and bridged ring dienes such as: tetrahydroindene;
- 10 methyltetrahydroindene; dicyclopentadiene; bicyclo-(2,2,1)hepta-2,5-diene; alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes such as 5-ethylidene-2-norbornene (ENB), 5-methylene-2-norbornene (MNB), 5-propyl-2-
- 15 norbornene, 5-isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, 5-cyclohexylidene-2-norbornene.

The amount of diene (wt. basis) in the copolymer could be from about 0% to 20% with 0% to 20 15% being preferred. The most preferred range is 0% to 10%.

Solvent may be utilized in the process but is optional. The monomer(s) can be dissolved prior to charging into the reactor or the monomer(s) can 25 act as a solvent also. Typically the concentration of the polymer product in the outlet stream should be 1 to 50%. Adventitious impurities deleterious to polymerization activity, especially in catalyst systems utilizing non-

30 coordinating anions, may be removed by the use of a group 13 element compound (as defined by the renumbered periodic table published in Chemical

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and Engineering News, 63(5), 27, 1985). Such impurity removal is described in U.S. Patent Application 496,378 (published as PCT International Publication PCT WO 91/14713).

- 5 The catalyst used in this process, the metallocene(s) catalyst and cocatalyst activator(s) are charged into the reactor through one or more separate inlet port or can be included in the monomer(s) stream. The metallocene
- 10 catalysts useful in this invention are monocyclopentadienyl transition metal complexes or biscyclopentadienyl transition metal complexes activated by an alumoxane or non-coordinating anion.
- 15 Once the monomer, solvent and the catalyst have been introduced into the reactor under polymerization conditions the product is removed in an outlet stream. The concentration of polymer product in the outlet stream should be 1 to 50%,
- 20 preferably 5 to 25%. The solvent may then be flashed off or removed by any other means known in the art. Typical solvents used in this process are linear, branched or aromatic hydrocarbons or mixtures of linear, branched or aromatic
- 25 hydrocarbons. Typical solvents include butane, pentane, isopentane, hexane, heptane, xylene toluene and benzene. Furthermore, mixtures of hydrocarbons include such products that are available under the trade names Aromatic 100;
- 30 Exxsol D40; Isopar C, E, G and H. Aromatic 100 is a mixed aromatic (0.3 percent paraffin and 99.7% aromatic(s) solvent available from Exxon

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Chemicals with a specific gravity of 0.873, a viscosity of 0.8 cP (centipoise) at 25°C. Aromatic 150 is a mixed aromatic solvent (0.2% paraffin and 99.8% aromatic(s)) available from Exxon Chemical which has a viscosity at 25°C centipoise of 1.2, a specific gravity of 0.895. Exxsol D40 is a dearomatized aliphatic solvent available from Exxon Chemical with a specific gravity of 0.779 viscosity of 1.0 at 25°C in centipoise, a composition of 49% paraffin, 51% cycloparaffin and less than 0.5% aromatics. The Isopar's are isoparaffins with viscosities between .5 and 1.6, specific gravities between 0.699 and 0.759 and compositions ranging from 100% paraffin and less than .1% cycloparaffin and .001% aromatic to 88% paraffin 12% cycloparaffin and less than 0.02% aromatic.

The polymer products produced by this invention differ from those previously produced in that it is possible using the metallocene catalyst and specific polymerization conditions to produce a tailored molecular weight distribution, a better comonomer incorporation and when using chiral metallocene catalyst, tailored stereoregularity. The polymers of this can be crystalline, semi-crystalline or amorphous products, for use as films, fibers, molded articles, adhesives, etc. The crystalline or semi-crystalline products of this invention behave as thermoplastic olefins and can be used in any application wherein crystalline thermoplastic olefins are used today, such as films, molded articles and adhesives. In

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particular the products of this invention will have improved toughness and strength. Elastomers produced by this process will exhibit improved strength and wear resistance. Improved clarity
5 will also be an attribute for products with high crystallinity.

For polymers of polyethylene crystallinity is controlled by varying the Molecular weight (Mw) and the weight percent of ethylene in the polymer.
10 In propylene however, crystallinity is dependent on catalyst selection.

Catalysts of this invention containing a metallocene component which is either a pure enantiomer or the racemic mixture of two
15 enantiomers of a rigid, chiral metallocene can polymerize prochiral olefins (propylene and higher α -olefins) to crystalline polymers including syndiotactic and isotactic polymers.

Bis(cyclopentadienyl) metal compounds in which
20 each of the cyclopentadienyl radicals is substituted and containing a covalent bridging group between the two cyclopentadienyl radicals or ones in which the substituents are chosen such that metallocene framework 1) has a C_2 axis of
25 symmetry through the metal center are particularly useful for isotactic polymerizations of this type. Such complexes, such as $Me_2Si(indenyl)_2ZrMe_2$ and $Me_2Si(tetrahydroindenyl)_2HfMe_2$ $Me_2Si(indenyl)(N-t-bu)ZrMe_2$ generally produces isotactic polymers
30 with higher degrees of stereoregularity than less symmetric chiral systems.

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Similarly, metallocene precursors providing tacticity control exist when (A-Cp) is (Cp)(Cp*), both Cp and Cp* having substituents on the cyclopentadienyl rings of sufficient bulk to
5 restrict rotation of the cyclopentadienyl rings such that the aforementioned symmetry conditions are satisfied.

Prochiral metallocenes for the production of syndiotactic polymers are those where (A-Cp) is
10 Cp-A'-Cp* and the substituents on Cp and Cp* is maximized and 2) there remains a plane of symmetry through the metal center and the carbon atoms on Cp and Cp* which are bonded to A'. For example, metallocenes based on complexes of propyl-2-
15 cyclopentadienyl-2-(1-fluorenyl) zirconium or $\text{Me}_2\text{Si}(1\text{-fluorenyl})(\text{NC}_6\text{H}_{11})\text{TiCl}_2$ can be used to polymerize propylene or higher α -olefins to syndiotactic polymers.

Specifically, the crystalline or semi-
20 crystalline products of this invention can be used in any TPO application such as molded articles, underhood applications, bumpers, exterior trim and interior trim, hose applications, facia, window trim, sound absorption, impact modifiers or window
25 damping of the like. The amorphous products of this invention are essentially elastomeric polymers and can be used as in any application or amorphous polymers are utilized. This invention specifically contemplate to production of ethylene
30 propylene rubbers and ethylene propylene diene rubbers. Specifically the elastomeric polymers of this invention can be used in application such as

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molded articles, fibers, films, laminates, coatings, extrusion coatings, rotomolding, blow molding, injection molding, blown cast film, adhesives, hot melt adhesives, pressure sensitive adhesives, wire and cable applications, food packaging and the like. In addition, polymers of this invention can also be plastomers, the term plastomers as used herein refers generally to a class of ethylene based copolymers with a density of less than about 0.900 g/cm^3 to about 0.865 g/cm^3 , a weight average molecular weight greater than about 20,000 (about 200 MI and lower). Plastomers have an ethylene crystallinity between plastics (i.e. linear low density and very low density polyethylenes) and ethylene alpha-olefins elastomers. In contrast VLDPE's typically have densities in the range of about 0.900 to about 0.915 g/cm^3 . Plastomers can be used as viscosity modifiers. Plastomers can be used as viscosity modifiers. Viscosity modifiers of this invention are random copolymers of ethylene, an alpha-olefin, and optionally a diene; alpha-olefin polymers, copolymers of alpha-olefins, or copolymers of an alpha-olefin, or mixtures thereof with a diene. Viscosity modifiers typically have a viscosity index of 100 to 400, and ignition point of at least 240°C , and a pour point of not more than 0°C .

Indeed, the process of this invention can also be used to produce other novel polymers and copolymers that have long chain branching. Another approach to LCB polyolefins utilizes the

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synthesis of an organoaluminum coiniciator made from a LDPE containing LCB. This method assumes that the polymeric aluminum cocatalyst will alkylate the titanium catalyst with the polymer chain. The alkylated Ti catalyst will then continue to polymerize ethylene onto the LDPE site effectively producing a LDPE-b-HDPE structure. Since the LDPE has LCB the resulting copolymer will also have LCB.

In accordance with the present invention, it has been discovered that soluble graft copolymers composed of a ethylene or propylene homopolymer or alpha-olefin copolymer backbone and a polyethylene sidechain can be controllably prepared when a macromonomer, specifically a vinyl terminated polyethylene, is copolymerized with ethylene or an alpha-olefin copolymer. The macromonomers suitable for this purpose are vinyl terminated and prepared via Ziegler polymerization of ethylene under conditions which favor lower molecular weight and vinyl termination: high temperatures; alkane solvents.

In addition we have found a catalyst system which can be thermally activated to produce vinyl terminated macromonomers; the same catalyst system efficiently copolymerizes the macromonomers with ethylene. We therefore believe

$\text{Me}_2\text{Si}(\text{Me}_4(5)(\text{NC}_{12}\text{H}_{23})\text{TiCl}_2$ activated by methylalumoxane to be useful in the direct synthesis (single reactor) of LCB HDPE.

Additionally we speculate that activation of other

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metallocenes by assorted activators may also lead to a thermally activated process.

The following examples are illustrative of the invention.

5 As is apparent from the foregoing description
the materials prepared in the procedures followed
relate to specific embodiments of the broad
invention. As apparent from the foregoing general
description and a specific embodiments that while
10 forms the invention have been illustrated and
described various modifications can be made
without departing from the spirit and scope of
this invention. Accordingly is not intended that
the invention be limited thereby.

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EXAMPLES

In the examples which illustrate the practice of the invention the analytical techniques described below were employed for the analysis of the resulting polyolefin products. Molecular weight determinations for polyolefin products were made by Gel Permeation Chromatography (GPC) according to the following technique. Molecular weights and molecular weight distributions were measured using a Waters 150 gel permeation chromatograph equipped with a differential refractive index (DRI) detector and a Chromatix KMX-6 on-line light scattering photometer. The system was used at 135°C with 1,2,4-trichlorobenzene as the mobile phase. Shodex (Showa Denko America, Inc.) polystyrene gel columns 802, 803, 804 and 805 were used. This technique is discussed in "Liquid Chromatography of Polymers and Related Materials III", J. Cazes editor, Marcel Dekker. 1981, p. 207, which is incorporated herein by reference. No corrections for column spreading were employed; however, data on generally accepted standards, e.g. National Bureau of Standards Polyethylene 1484 and anionically produced hydrogenated polyisoprenes (an alternating ethylene-propylene copolymer) demonstrated that such corrections on Mw/Mn (= MWD) were less than 0.05 units. Mw/Mn was calculated from elution times. The numerical analyses were performed using the commercially available Beckman/CIS customized LALLS software in

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conjunction with the standard Gel Permeation package, run on a HP 1000 computer.

Calculations involved in the characterization of polymers by ^{13}C NMR follow the work of F. A. Bovey in "Polymer Conformation and Configuration" Academic Press, New York, 1969.

A. Preparation of $\text{B}(\text{C}_6\text{F}_5)_3\text{Q}^-$ Activators

In general the anionic complexes of the form $[\text{B}(\text{pfp})_3\text{Q}]^-$ can be prepared by the addition of the lithium or Grignard reagents $\text{Li}[\text{Q}]$ or $\text{MgBr}[\text{Q}]$ to $\text{B}(\text{pfp})_3$ in ether from which reaction $\text{Li}[\text{B}(\text{pfp})_3\text{Q}]^-$ is isolated in high yield as an etherate. The lithium salt can be converted into the final ammonium salt by treatment with $\text{R}_3\text{NH}^+\text{Cl}^-$ in methylene chloride. The insoluble lithium chloride is removed by filtration and the excess ammonium chloride is removed by washing the methylene chloride solution with water. The methylene chloride solution is dried using Na_2SO_4 , filtered and concentrated to the point of crystallization. Addition of a counter solvent such as pentane can be used to precipitate.

B. Preparation of monocyclopentadienyl metallocene complexes is discussed in U.S. Patent 5,096,867, issued March 17, 1992; and U.S. Patent 5,055,438, issued October 8, 1991, which are both incorporated by reference as if fully set forth.

C. Preparation of bis-cyclopentadienyl complexes is described in co-pending USSN 752,415 originally USSN 501,688, filed June 6, 1983) which is equivalent to Canadian Patent 1,260,490 granted

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September 26, 1989 and is herein fully incorporated by reference as is fully set forth.

Examples 1-6 of Polymerization

Example 1

5 Polymerization-Me₂Si(Me₄C₅)(NC₁₂H₂₃)TiCl₂/MAO

 The polymerization run was performed in a 1-liter autoclave reactor equipped with a paddle stirrer, an external water jacket for temperature control, a regulated supply of dry nitrogen, ethylene, propylene, 1-butene and hexane, and a septum inlet for introduction of other solvents or comonomers, transition metal compound and alumoxane solutions. The reactor was dried and degassed thoroughly prior to use. A typical run consisted of injecting 300 ml of toluene, 100 ml of 1-butene, 5 ml 1.0 M MAO (methylalumoxane), 2.68 mg of Me₂Si(Me₄C₅)NC₁₂H₂₃)TiCl₂ (2.0 ml of a 13.4 mg in 10 ml of toluene solution) into the reactor. The reactor was heated to 80°C and the ethylene (65 psi) was introduced into the system. The polymerization reaction was limited to 30 minutes. The reaction was ceased by rapidly cooling and venting the system. The solvent was evaporated off of the polymer by a stream of nitrogen. An ethylene-butene copolymer was recovered (90.2 g, MW = 75,500, MWD = 1.94, 43.7 mole % butene).

Example 2

30 Polymerization-Me₂Si(Me₄C₅)(NC₁₂H₂₃)TiCl₂/MAO

 Using the same reactor design and general procedure already described, 500 ml of toluene, 8 ml of 1-hexane, 3.0 ml of 1.0 M MAO, and 1.34 mg

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of $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{NC}_{12}\text{H}_{23})\text{TiCl}_2$ (1.0 ml of a 13.4 mg in 10 ml of toluene solution) were added to the reactor. The reactor was heated to 90°C, the ethylene was introduced (180 psi), and the reaction was allowed to run for 15 minutes, followed by rapidly cooling and venting the system. After evaporation of the solvent, 37.3 g of an ethylene-hexane copolymer was recovered (MW = 220,600, MWD = 2.91, 1.8 mole % hexane).

Example 3

Polymerization - $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{NC}_{12}\text{H}_{23})\text{TiCl}_2/\text{MAO}$

Using the same reactor design and general procedure already described, 500 ml of toluene, 3.0 ml of 1.0 M MAO, and 1.34 mg of compound $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{NC}_{12}\text{H}_{23})\text{TiCl}_2$ (1.0 ml of a 13.4 mg in 10 ml of toluene solution) were added to the reactor. The reactor was heated to 100°C, the ethylene was introduced (40 psi), and the reaction was allowed to run for 30 minutes, followed by rapidly cooling and venting the system. After evaporation of the solvent, 5.5 g of polyethylene was recovered (MW = 161,100, MWD = 3.27).

Example 4

Polymerization - $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{NC}_{12}\text{H}_{23})\text{TiCl}_2/\text{MAO}$

Using the same reactor design and general procedure already described, 45 ml of toluene, 50 ml styrene (inhibitor removed), 2.0 ml of 1.0 M MAO, and 1.34 mg of compound $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{NC}_{12}\text{H}_{23})\text{TiCl}_2$ (1.0 ml of a 13.4 mg in 10 ml of toluene solution) were added to the reactor. The reactor was heated to 90°C, ethylene was introduced (180 psi), and the reaction was

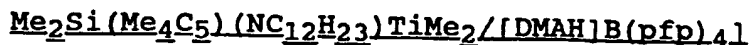
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allowed to run for 60 minutes, followed by rapidly
cooling and venting system. After evaporation of
the solvent, 10.2 g of an ethylene-styrene
copolymer was recovered (MW = 71,200, MWD = 1.87,
5 33 mole % styrene). GPC indicated that a small
fraction of polystyrene was also present (MW =
9400, MWD = 1.64).

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Example 5

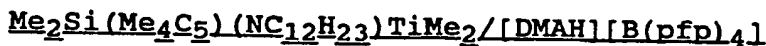
Polymerization -



Using the same reactor design and general
 5 procedure already describe, 400 ml propylene, and
 20 ml of catalyst solution (40 mg
 $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{NC}_{12}\text{H}_{23})\text{TiMe}_2$ and 4 mg
 $[\text{DMAH}][\text{B}(\text{pfp})_4]$ in 20 ml of toluene) were added to
 the reactor. The reactor was heated to 50°C and
 10 the reaction was allowed to run for 25 minutes,
 followed by rapidly cooling and venting the
 system. After evaporation of the solvent, 11.7 g
 of atactic polypropylene was recovered (MW =
 667,300, MWD = 2.28).

15 Example 6

Polymerization -



Using the same reactor design and general
 procedure already described, 400 ml propylene, and
 20 3 ml of catalyst solution (30 mg
 $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{NC}_{12}\text{H}_{23})\text{TiMe}_2$ and 15 mg
 $[\text{DMAH}][\text{B}(\text{pfp})_4]$ in 10 ml of toluene) were added to
 the reactor. The reactor was heated to 50°C, the
 ethylene was introduced (100 psi), and the
 25 reaction was allowed to run for 15 minutes,
 followed by rapidly cooling and venting the
 system. After evaporation of the solvent, 4.0 g
 of an ethylene-propylene copolymer was recovered
 (MW = 552,700, MWD = 4.08 mole % propylene).

30 Example 7

Catalyst Preparation:

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In a 2000 ml flask, Davison 948 silica (dried at 800°C, 150 g) was slurried in pentane (600 ml). To this slurry was added triethylaluminum (1.5 M in heptane, 200 ml). After stirring for 30 minutes, 150 ml of the solution was decanted and additional triethylaluminum solution (100 ml) added. After an additional 30 minutes, the solids were filtered off, washed with pentane, and dried.

The treated silica was slurried in toluene (500 ml). To this was added a solution of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron (6 g) in warm toluene (900 ml). The toluene was evaporated in a vacuo to yield a free-flowing solid.

The solid was slurried in pentane (700 ml) and to it was added a solution of bis(cyclopentadienyl)hafnium dimethyl (3 g) in pentane (200 ml). The pentane was evaporated in vacuo to give a light beige solid.

Polymerization:

A 250 mg sample of the above catalyst was flushed into a 1 L stainless-steel autoclave containing isobutane (400 ml), 1-octene (50 ml), and ethylene (150 psi). The autoclave was stirred and heated at 60°C for 30 minutes, then vented and cooled. The yield of ethylene-octene copolymer was 13.4 g. The polymer had a molecular weight of 518,000, a molecular weight distribution of 3.5, and contained 5.03 mole percent octene.

Example 8

Supported N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron was prepared as

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in Example A. A 500 mg sample was reacted with bis(cyclopentadienyl)hafnium dimethyl (9 mg) in pentane. The pentane was evaporated to give a supported catalyst.

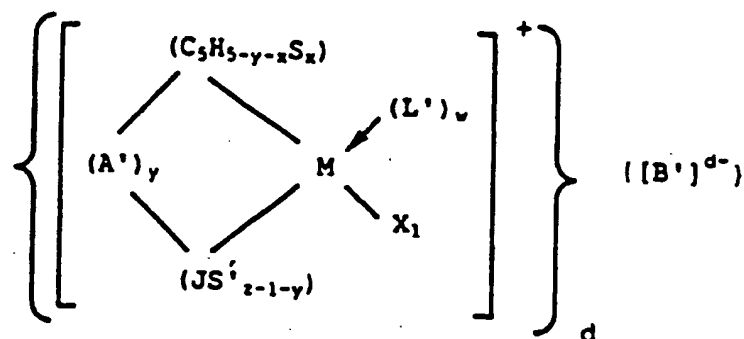
- 5 A 300 mg sample of the above catalyst was flushed into a 1 L stainless-steel autoclave containing hexane (150 ml), 1-octene (150 ml), and ethylene (150 psi). The autoclave was stirred and heated at 80°C for 55 minutes, then vented and
- 10 cooled. The yield of ethylene-octene copolymer was 1.8 g. The polymer had a molecular weight of 158,000, a molecular weight distribution of 2.5, and contained 16.07 mole percent octene.

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Claims

- 1 1. A process for the solution phase
2 polymerization of olefins comprising:
3 contacting in a solvent olefins or mixtures
4 of olefins with a metallocene compound and a
5 cocatalyst activator in one or more continuous
6 stirred tank or tubular reactors connected in
7 series or parallel.
- 1 2. The process of claim 1, wherein the olefins
2 or mixture of olefins have 2 to 100 carbon atoms.
- 1 3. The process of claim 1, wherein the olefins
2 or mixture of olefins are α -olefins.
- 1 4. The process of claim 2, wherein the olefins
2 comprise ethylene or propylene or a mixture
3 thereof.
- 1 5. The process of claim 1, wherein the mixture
2 of olefins comprises ethylene, propylene and a
3 non-conjugated diene.
- 1 6. The process of claim 1, wherein the mixture
2 of olefins comprises cyclic or linear olefins
3 containing one or more aromatic rings.
- 1 7. The process of claim 1, wherein the mixture
2 of olefins comprises propylene, butene, hexene,
3 octene or dodecene.
- 1
2 8. The process of claim 1, wherein the
3 metallocene catalyst is represented by the
4 formulae:
5 (1) $[[[(A-Cp)MX_1]^+]_d] \{[B']^{d-}\}$
6 (2) $[[[(A-Cp)MX_1L]^+]_d] \{[B']^{d-}\}$
7 (3)
8

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wherein:

(A-Cp) is either (Cp) (Cp*) or Cp-A'-Cp*; Cp and Cp* are the same or different cyclopentadienyl rings substituted with from zero to five substituent groups S, each substituent group S being, independently, a radical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted pnictogen, substituted chalcogen or halogen radicals, or Cp and Cp* are cyclopentadienyl rings in which any two adjacent S groups are joined forming a C₄ to C₂₀ ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

A' is a bridging group, which group may serve to restrict rotation of the Cp and Cp* rings or (C₅H₅-y-xS_x) and JS' (z-1-y) groups;

(C₅H₅-y-xS_x) is a cyclopentadienyl ring substituted with from zero to five S radicals;

x is from 1 to 5 denoting the degree of substitution;

M is titanium, zirconium or hafnium;

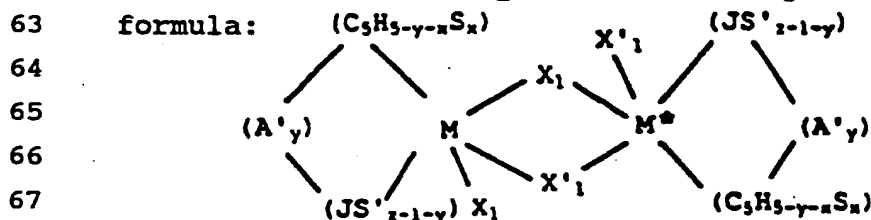
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40 X_1 is a hydride radical, hydrocarbyl radical,
 41 substituted-hydrocarbyl radical, hydrocarbyl-
 42 substituted organometalloid radical or halocarbyl-
 43 substituted organometalloid radical which radical
 44 may optionally be covalently bonded to both or
 45 either M and L or all or any M, S or S';

46 (JS'_{z-1-y}) is a heteroatom ligand in which J
 47 is an element from Group 15 of the Periodic Table
 48 of Elements with a coordination number of 3 or an
 49 element from Group 16 with a coordination number
 50 of 2; S is a radical group which is a hydrocarbyl,
 51 substituted hydrocarbyl, halocarbyl, substituted
 52 halocarbyl, hydrocarbyl-substituted
 53 organometalloid, or halocarbyl-substituted
 54 organometalloid; and z is the coordination number
 55 of the element J;

56 y is 0 or 1;

57 L' is an olefin, diolefin or aryne ligand, or
 58 a neutral Lewis base or a second transition metal
 59 compound of the same type such that the two metal
 60 centers M and M^* are bridged by X_1 and X'_1 ,
 61 wherein M^* has the same meaning as M and X'_1 has
 62 the same meaning as X_1 , represented by the
 63 formula:



68 w is an integer from 0 to 3;

69 B' is a chemically stable, non-nucleophilic
 70 anionic complex having a molecular diameter about
 71 or greater than 4 angstroms or an anionic Lewis-

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72 acid activator; provided that when B' is a Lewis-
73 acid activator, X₁ can also be an alkyl group
74 donated by the Lewis-acid activator; and

75 d is an integer representing the charge of B.

1 9. The process of claim 7, wherein the activator
2 is represented by the formulae:

3 $(R-Al-O)_n$ or

4 $R(R-Al-O)_nAlR_2$,

5 where R is a C₁ to C₆ alkyl group such as, for
6 example, methyl, ethyl, propyl, butyl and pentyl,
7 n is an integer of from 3 to 20, and n' is an
8 integer from 1 to 20.

1 10. The process of claim 7, wherein the activator
2 is represented by the formulae:

3 $[(L'-H)^+]^{d+}[(M')^{m+}Q_1Q_2\cdots Q_n]^{d-}$

4 wherein:

5 H is a hydrogen atom;

6 $[L'-H]$ is a Bronsted acid;

7 M' is a metal or metalloid;

8 Q₁ to Q_n are, independently, hydride
9 radicals, hydrocarbyl and substituted-hydrocarbyl
10 radicals, halocarbyl and substituted-halocarbyl
11 radicals and hydrocarbyl- and halocarbyl-
12 substituted organometalloid radicals,
13 disubstituted pnictogen radicals, substituted
14 chalcogen radical and any one, but not more than
15 one, of Q₁ to Q_n may be a halogen radical.

1 11. A product produced by the process of claim 1.

1 12. An elastomer produced by the process of claim
2 1.

1 13. A copolymer produced by the process claim 1.

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- 1 14. The process of claim 1, wherein the product
2 is molded into an article.
- 1 15. The process of claim 1, further comprising a
2 maximum reactor temperature of 350°C, a minimum inlet
3 temperature of -40°C, a maximum outlet temperature
4 of 350°C, and a maximum pressure of 340 atm.

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C08F10/00; C08F2/06; C08F4/60																				
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched⁷</div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%; padding: 5px;">Classification System</th> <th style="padding: 5px;">Classification Symbols</th> </tr> <tr> <td style="padding: 5px;">Int.Cl. 5</td> <td style="padding: 5px;">C08F</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched⁸</div>			Classification System	Classification Symbols	Int.Cl. 5	C08F														
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III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; padding: 5px;">Category⁹</th> <th style="width: 70%; padding: 5px;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 20%; padding: 5px;">Relevant to Claim No.¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">P,X</td> <td style="padding: 5px;"> WO,A,9 305 082 (BASF) 18 March 1993 see the whole document <div style="text-align: right;">---</div> </td> <td style="text-align: center; vertical-align: top; padding: 5px;"> 1-7,9, 11-15 </td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;"> WO,A,9 104 257 (EXXON) 4 April 1991 see page 22, line 9 - line 29; claims; figures 1-9; example 55 <div style="text-align: right;">---</div> </td> <td style="text-align: center; vertical-align: top; padding: 5px;"> 1-7,8,9, 11-15 </td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;"> WO,A,8 802 009 (EXXON) 24 March 1988 see the whole document <div style="text-align: right;">---</div> </td> <td style="text-align: center; vertical-align: top; padding: 5px;"> 1-9, 11-15 </td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;"> EP,A,0 260 999 (EXXON) 23 March 1988 see the whole document <div style="text-align: right;">---</div> </td> <td style="text-align: center; vertical-align: top; padding: 5px;"> 1-9, 11-15 </td> </tr> <tr> <td colspan="2" style="text-align: center; padding: 5px;">-/--</td> <td></td> </tr> </tbody> </table>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	P,X	WO,A,9 305 082 (BASF) 18 March 1993 see the whole document <div style="text-align: right;">---</div>	1-7,9, 11-15	X	WO,A,9 104 257 (EXXON) 4 April 1991 see page 22, line 9 - line 29; claims; figures 1-9; example 55 <div style="text-align: right;">---</div>	1-7,8,9, 11-15	X	WO,A,8 802 009 (EXXON) 24 March 1988 see the whole document <div style="text-align: right;">---</div>	1-9, 11-15	X	EP,A,0 260 999 (EXXON) 23 March 1988 see the whole document <div style="text-align: right;">---</div>	1-9, 11-15	-/--		
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>⁹ Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>																				
IV. CERTIFICATION <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;"> Date of the Actual Completion of the International Search <div style="text-align: center; font-weight: bold;">05 OCTOBER 1993</div> </td> <td style="width: 50%; padding: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold;">20. 10. 93</div> </td> </tr> <tr> <td style="width: 50%; padding: 5px;"> International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div> </td> <td style="width: 50%; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center; font-weight: bold;">DE ROECK R.G.</div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center; font-weight: bold;">05 OCTOBER 1993</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold;">20. 10. 93</div>	International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center; font-weight: bold;">DE ROECK R.G.</div>														
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	DE,A,3 150 270 (EC ERDÖLCHEMIE) 30 June 1983 see the whole document -----	1-9, 11-15

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
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US 9306052
SA 76183

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